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In this review, the second in a series, the viscosity–molecular weight (Mark–Houwink–Sakurada) relationships have been critically evaluated for atactic polystyrene for a variety of solvents often used for viscosity measurements. These are benzene, toluene, 1,2,4-trichlorobenzene, tetrahydrofuran, o-dichlorobenzene, 2-butanone, and two theta solvents, cyclohexane and decalin. In addition, the Mark–Houwink–Sakurada parameters for several other solvents, not used as frequently, are provided.

Key words: benzene; 2-butanone; cyclohexane; decalin; o-dichlorobenzene; Mark–Houwink; molecular weight; size exclusion chromatography; tetrahydrofuran; toluene; 1,2,4-trichlorobenzene; viscosity.

1. Introduction

The number of papers in the literature providing intrinsic viscosity–molecular weight data for polystyrene is extremely large, in contrast to the case of polyethylene,[1] with most of the data having been obtained before 1970. Despite the fact that absolute methods for determining molecular weight were well developed by that time, a large fraction of the Mark–Houwink (or Mark–Houwink–Sakurada) relations reported in the literature depend on molecular weights which were determined indirectly. In some cases molecular weights were first determined by viscosity measurements in some other solvent for which the Mark–Houwink relation had already been established. Some authors used molecular weights provided by the vendor of the polymer with no indication of how they were obtained. As stated in the first report in this series, this uncertainty adds another source of error to the Mark–Houwink parameters K and a, so that relationships derived using molecular weights obtained by absolute methods are preferred.

The data for seven commonly used solvents have been evaluated, and for each a recommended relation between intrinsic viscosity ([η]) and molecular weight is given. In the case of both benzene and toluene, a quadratic relation rather than a linear one is suggested for log[η] versus log M. The other solvents are 1,2,4-trichlorobenzene, o-dichlorobenzene, 2-butanone, tetrahydrofuran, and cyclohexane. The last is a theta solvent.

Mark–Houwink parameters for several other solvents that are not used as frequently, are also given. These are decalin, 1,2-dichloroethane, chloroform, p-dioxane, dimethyl formamide, ethyl benzene, N-methylpyrrolidone,

and tetrachloroethane. In some cases only one set of data could be found for a solvent.

The papers concerned with the viscosity–molecular weight relationships of polystyrene are too numerous for all to be listed, and only those cited in the text are referenced.

2. The Mark–Houwink Constants for Polystyrene in Various Solvents

2.1. Benzene

Once it became possible to synthesize polystyrene anionically to give narrow molecular weight distribution polymers, a spate of papers appeared reporting the viscosity of these materials over a wide molecular weight range. The data examined in this study is derived about evenly between earlier studies using well fractionated samples and those synthesized anionically.

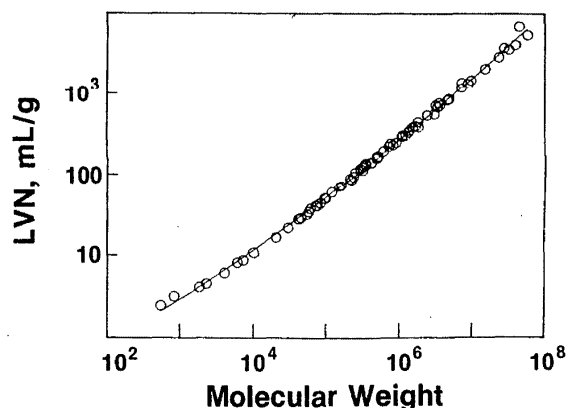The Mark–Houwink relation [η] $= KM^a$ is an empiri-

FIG. 1. Composite plot of the polystyrene–benzene data referred to in Table 1. Log of the limiting viscosity number (LVN) or the intrinsic viscosity is plotted against log of the molecular weight.

TABLE 1. Sources of benzene data

Author	$T/°C$	$K/$ (10^{-3} mL/g)	a	No. of samples	MW range	MW method	Ref.
Fukuda et al.	25			6	310 000–4.6×10⁶	light scattering	2
Altares et al.	25			6	540–7200	various methods	3
	.			12	4 500–820 000	cyclohexane viscosity	
Slagowski	40			5	411 000–44×10⁶	light scattering	4
Yamaguchi et al.	35			5	1.8×10⁶–7.1×10⁶	light scattering	5
Inagaki et al.	30			10	58 000–7.1×10⁶	light scattering	6
Krigbaum and Flory	25	9.52	0.744	6	30 000–607 000	osometry	7
Yamamoto et al.	30	11.5	0.73	4	246 000–2.9×10⁶	light scattering	8
Bawn et al.	25	11.3	0.73	6	72 000–900 000	osometry	9
Einaga et al.	25	7.8	0.75	15	4 000–56×10⁶	light scattering and supplier values	10

cal one and there is no *a priori* reason to expect the same values of K and a to hold over a very large range of molecular weight. Although no single set of reported data covers five or six decades of molecular weight, it was possible to do so by combining several sets. The result shown in Fig. 1 is a single curve which is best fit by a quadratic equation,

$$\log[\eta] = A + B \log M + C (\log M)^2,$$ (1)

where

$A = -0.686,$ s.d. 0.064;

$B = 0.272,$ s.d. 0.025;

$C = 0.0408,$ s.d. 0.0024;

with $[\eta]$ in mL/g.

This relation is for 55 degrees of freedom with a residual standard deviation of 0.027 or about 6% and is preferred over a linear fit with a residual standard deviation of 0.069 or 16%. The data span a six-decade range from molecular weights of 540 to 44×10⁶. In Table 1 are listed the authors, number of samples, molecular weight range, and the method of determining molecular weights, as well as the author's value of K and a when given. Despite the fact that temperatures were not the same for all sets of data, the results in Fig. 1 show that the effect of temperature is small. Apparently, the samples, whether anionically prepared or fractions, had a sufficiently narrow molecular weight distribution so that all points fell on the same curve. This would not necessarily be the case, as shown in the first paper of this series,[1] for broader distributions, if the data were obtained in some cases by osmotic pressure to give number average molecular weight, and in others by light scattering to give weight average molecular weight. Some of the data in the papers listed in Table 1 were not used if the viscosities for samples over 1 000 000 in molecular weight were not determined at low shear rates.

It is of interest to calculate the slope of the curve at various molecular weights:

Molecular weight	Slope
1 000	0.517
10 000	0.598
100 000	0.680
1 000 000	0.761

Thus, if the Mark–Houwink exponent is calculated in the ordinary way by assuming a linear $\log[\eta]$–$\log M$ relation, the exponent or slope will depend on the range selected for its determination.

Dondos and Benoit[11] have proposed representing viscosity data by a different relationship, namely, by plotting $1/[\eta]$ versus $1/M^{1/2}$ to give a straight line. However, as the authors point out, "it is only useful for the low and medium molecular weight range since at high molecular weights the points are crowded near the origin." Since it is important for this report that the entire range of molecular weight be represented as well as possible, a second-order polynomial is used.

2.2. Toluene

Just as in the case of benzene, a very large amount of information is available for toluene over a considerable molecular weight range. It is possible to select papers in which molecular weights were determined by absolute methods. In Fig. 2 the data reported in eight different papers are plotted over a range of molecular weights from 660 to 4×10⁶. The
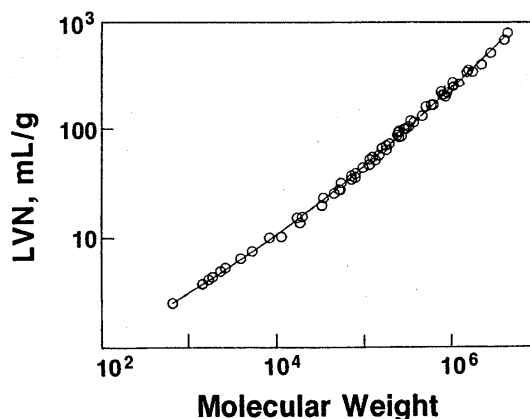

FIG. 2. Composite plot of the polystyrene–toluene viscosity data referred to in Table 2.

TABLE 2. Sources of toluene data

Author	$T/°C$	$K/$ (10^{-3} mL/g)	a	No. of samples	MW range	MW method	Ref.
McCormick	25	9.77	0.73	12	11 400–1.06×10⁶	sedimentation velocity	12
Berry	12			9	20 000–4.4×10⁶	light scattering	13
Rossi et al.'	25			11	660–34 500	cryoscopy	14
Yamamoto et al.	30	8.81	0.75	5	280 000–765 000	light scattering	8
Papazian	25	8.5	0.74	5	49 000–242 000	light scattering	15
Oth and Desreux	25	7.50	0.75	7	115 000–2.8×10⁶	light scattering	16
Bawn et al.	25	13.4	0.71	5	72 000–1.5×10⁶	osmotic pressure	9
Nakata	35	12.6	0.71	15	33 000–3.2×10⁶	light scattering	17

TABLE 3. Mark–Houwink constants—polystyrene in 1,2,4-trichlorobenzene

Author	$T/°C$	$K/$ (10^{-3} mL/g)	a	No. of samples	MW range	MW method	Ref.
Otocka et al.	135			8	4 800–1.8×10⁶	unpublished	19
Coll and Gilding	135	12.1	0.707	10	10 300–1.67×10⁶	unpublished	20
Williamson and Cervenka	135	17.2	0.67	10	2 200–1.8×10⁶	unpublished	21
Boni et al.	130	8.95	0.727	7	3 500–860 000	vapor pressure, osmometry, membrane osmometry, light scattering, ultra centrifugation	22

curve is also best fit by a quadratic equation,

$$\log[\eta] = A + B \log M + C (\log M)^2, \qquad (2)$$

where

$A = -0.538,$ s.d. 0.075;

$B = 0.203,$ s.d. 0.0321;

$C = 0.0471,$ s.d. 0.0033;

with $[\eta]$ in mL/g and for 66 degrees of freedom and a residual standard deviation of 0.026 or 6%. A linear fit, on the other hand, would give a 14% standard deviation.

The sources of the data are listed in Table 2. It is interesting to note that Berry's data for 12 °C fall on the same curve as the data taken at 25–30 °C. Most of the data were obtained from papers in which fractionated samples were employed because so much of the work was carried out before the advent of anionic polymerization.

2.3. 1,2,4-Trichlorobenzene

The Mark–Houwink relation in 1,2,4-trichlorobenzene is of special importance because this solvent is the one most frequently used for the analysis of polyolefins, particularly polyethylene, in size exclusion chromatography (GPC). Because these analyses must be carried out at an elevated temperature, Mark–Houwink constants for polystyrene, the reference polymer for the Universal Calibration method,[18] have been determined at 130 and 135 °C in this solvent. However, it is now recognized that the higher molecular weight polystyrenes—those over 1 000 000—tend to degrade at elevated temperature in trichlorobenzene. This may account for the generally better agreement in the published

Mark–Houwink relations at the lower molecular weights than at the higher ones.

Although those Mark–Houwink relations are preferred where the molecular weights are determined by absolute methods, only one set of data meeting this criterion could be found, namely, that of Boni et al.[22] A complete evaluation of the results of the other authors listed in Table 3 could not be carried out because the sources of their molecular weight data are not given. Nevertheless, when all four sets of data are plotted together as shown in Fig. 3, the points fall on a single curve from which K and a are determined. Both the quadratic and the linear fits to the composite curve have the same residual standard deviation of 0.035 or 8%. Choosing
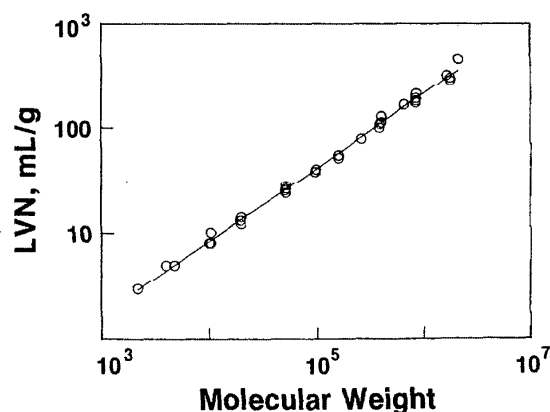

FIG. 3. Composite plot of the 130–135 °C polystyrene–trichlorobenzene viscosity data of Table 3.

the simpler linear fit, we obtain

$$[\eta] = 14.6 \times 10^{-3} M^{0.689} \quad \text{mL/g at 135 °C}, \qquad (3)$$

in the molecular weight range of 5000 to 1.8×10^6 g/mol with 32 residual degrees of freedom.

2.4. Tetrahydrofuran (THF)

The Mark–Houwink relation for this solvent is also of special importance because it is the most commonly used solvent in size exclusion chromatography (GPC), for which K and a are needed for calibration using the Universal Calibration technique. Although there are some 30 papers concerned with polystyrene in THF, there are very few in which absolute determinations of molecular weight were carried out. Hence, the relation proposed by Benoit et al.,[23] for which the absolute molecular weights were determined by light scattering, is recommended,

$$[\eta] = 14.1 \times 10^{-3} M^{0.70} \quad \text{mL/g at 25 °C}, \qquad (4)$$

in the molecular weight range of 13 000 to 2.2×10^6 g/mol.

The data of LePage et al.[24] also fit this relationship well, but this is not the case for the data of Boni et al.[22] with $K = 6.82 \times 10^{-3}$ mL/g and $a = 0.766$ in the narrower molecular weight range of 50 000–860 000.

It has been noted by Spychaj et al.[25] that the contamination of THF with water lowers the viscosity values substantially and the mixture behaves as a theta solvent. For a sample of 2×10^6 molecular weight, the viscosity decreased to as little as one-third of the original value at a water content of 8%.

2.5. o-Dichlorobenzene

Several workers employ o-dichlorobenzene instead of 1,2,4-trichlorobenzene as the solvent for polyethylene in size exclusion chromatography and thus require the Mark–Houwink relation for polystyrene in this solvent for calibration. The best available data are those of Dawkins and Maddock,[26] who did not measure the molecular weights of the polystyrene directly but depended on the supplier's values.
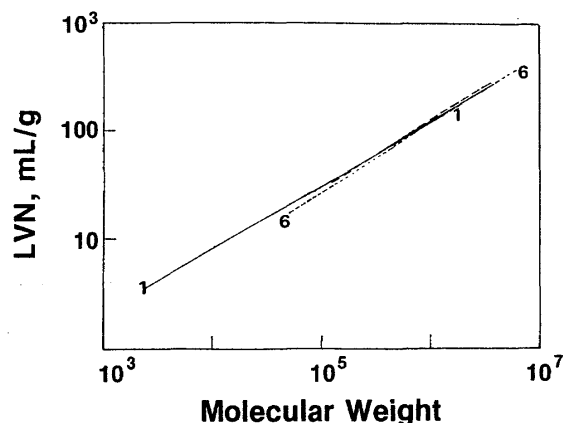
FIG. 4. Log limiting viscosity number vs log molecular weight of polystyrene in butanone. Solid line, labeled 1, are data of Outer, Carr and Zimm (Ref. 27). Data of Nakata (Ref. 17), labeled 6, are shown as dotted line. Data of Bawn et al. (Ref. 9), Oth and Desreux (Ref. 16), Oyama et al. (Ref. 28), and Bianchi et al. (Ref. 29) are shown as dashed lines.

They obtained

$$[\eta] = 13.8 \times 10^{-3} M^{0.7} \quad \text{mL/g at 138 °C}, \qquad (5)$$

in the molecular weight range of 20 000–411 000.

Of the few results reported and available in the literature, these appear to be the most comprehensive.

2.6. 2-Butanone (Methyl Ethyl Ketone)

The Mark–Houwink relation of Outer, Carr, and Zimm,[27] which is derived from data from 19 fractions, agrees with the results of many later workers in the higher molecular weight region. The curve in Fig. 4, labeled 1, representing the Outer et al. data is essentially coincident with the data of Bawn et al.,[9] Oth and Desreux,[16] and Oyama et al.[28] However, the relation derived by Nakata,[17] which extends to somewhat lower molecular weights though not as low as that of Outer et al. (curve 6), begins to deviate substantially at these lower molecular weights, chiefly because of the larger value of a. Since the Outer et al. data are more exten-

TABLE 4. Mark–Houwink constants for infrequently used solvents

Solvent Author	$T/°C$	$K/$ (10^{-3} mL/g)	a	Range	Ref.
Dichloroethane					
Outer, Carr, and Zimm	22	0.21	0.66	3 000–1.7×10^6	27
Nakata	35	14.3	0.69	44 000–4.2×10^6	17
Chloroform					
Oth and Desreux	25	7.16	0.76	115 000–2.8×10^6	16
Bawn et al.	25	11.2	0.73	72 000–1.8×10^6	9
Dioxane					
Bianchi et al.	34	15	0.694	10 000–685 000	29
N,N-dimethyl formamide					
Tsimpris et al.	25–45	31.8	0.603	10 000–864 000	30
Ethyl benzene					
Bawn et al.	25	17.6	0.68	72 000–1.5×10^6	9
N-methyl pyrrolidone					
Peureux and Lochon	85	12	0.72	20 000–2×10^6	31
Tetrachloroethane					
Peureux and Lochon	50	11.5	0.73	20 000–2×10^6	31

TABLE 5. Values of K for polystyrene in cyclohexane

Author	No. of samples	$K/(10^{-3}$ mL/g)	MW range	MW method	Ref.
Fukuda et al.	9	87.7	310 000–9.7×10⁶	light scattering	2
Inagaki et al.	13	84.6	58 000–7.1×10⁶	light scattering	6
Berry	19	84.0	198 000–4.4×10⁶	light scattering	13
Yamamato et al.	5	91	252 000–2.9×10⁶	light scattering	8

TABLE 6. Values of K for polystyrene in decalin

Author	$\theta/°C$	$K/(10^{-3}$ mL/g)	MW range	No. of samples	Ref.
cis-Decalin					
Berry	12.2	82.4	19 000–4.4×10⁶	6	13
trans-Decalin					
Fukuda et al.	20.4	80.5	310 000–9.7×10⁶	8	2

sive, including 12 points below the region measured by Nakata, the Mark–Houwink parameters of the former are preferred. Hence the recommended relation for 2-butanone is

$$[\eta] = 39 \times 10^{-3} M^{0.58} \text{ mL/g at 25 °C}, \tag{6}$$

in the molecular weight range of 2500 to 1.8×10^6.

2.7. Chloroform

Mark–Houwink relations for polystyrene in chloroform have been reported both by Oth and Desreux[16] as well as by Bawn et al.[9] Since Oth and Desreux determined molecular weights directly by osmotic pressure and light scattering their relation is the recommended one,

$$[\eta] = 7.16 \times 10^{-3} M^{0.76} \text{ mL/g at 25.0 °C},$$

in the molecular weight range 115 000 to 2.8×10^6.

2.8. Dichloroethane

Of the two available determinations of the Mark–Houwink relation for polystyrene in dichloroethane, the one by Outer, Carr, and Zimm[27] is preferable to the one by Nakata[17] because a wider molecular weight range is covered. If the two Mark–Houwink lines are plotted together, very little difference is observable despite the fact that the Outer et al. data is for 22 °C whereas the Nakata data is for 35 °C. The K

and a values for both are listed in Table 4. The preferred Outer, Carr, and Zimm relation is

$$[\eta] = 0.021 M^{0.66} \text{ mL/g at 22 °C},$$

in the 3000 to 1.7×10^6 molecular weight range.

2.9. Cyclohexane

Cyclohexane, a theta solvent for polystyrene at 34.5 °C is very often employed for viscosity measurements for the determination of molecular weight because of the certainty of the square-root dependence on the molecular weight at the theta temperature,

$$[\eta] = KM^{1/2}. \tag{7}$$

A reliable value of K, however, is still required. The results of four different authors, obtained in each case by equally satisfactory procedures, yield a weighted average value for K of 85.7×10^{-3} mL/g at the theta temperature, 34.5 °C. This average value of K was obtained by weighting the individual K values by the number of samples in each determination. As shown in Table 5 the molecular weights range from 58 000 to almost 10 000 000.

Papazian[15] determined the Mark–Houwink relation for cyclohexane at 50 °C, some 15° above the theta temperature.

TABLE 7. Recommended viscosity–molecular weight relation for atactic polystyrene

Solvent	$T/°C$	Equation
Benzene	25–40	$\log[\eta] = -0.686 + 0.272 \log M + 0.0408 (\log M)^2$
Toluene	12–30	$\log[\eta] = -0.538 + 0.203 \log M + 0.0471 (\log M)^2$
1,2,4-Trichlorobenzene	135	$[\eta] = 14.6 \times 10^{-3} M^{0.689}$
Tetrahydrofuran	25	$[\eta] = 14.1 \times 10^{-3} M^{0.70}$
o-Dichlorobenzene	138	$[\eta] = 13.8 \times 10^{-3} M^{0.7}$
2-Butanone	25	$[\eta] = 39 \times 10^{-3} M^{0.58}$
Cyclohexane	34.5 (θ)	$[\eta] = 85.7 \times 10^{-3} M^{0.5}$
cis-Decalin	12.2 (θ)	$[\eta] = 82.4 \times 10^{-3} M^{0.5}$
trans-Decalin	20.4 (θ)	$[\eta] = 80.5 \times 10^{-3} M^{0.5}$

The molecular weights of seven anionically produced polystyrene ranging in molecular weight from 4500 to 510 000 were determined by light scattering. He found

$$[\eta] = 36.4 \times 10^{-3} M^{0.584} \quad \text{mL/g at 50 °C.} \tag{8}$$

2.10. Decalin

Decalin, also a θ solvent for polystyrene, has two isomeric forms, cis-decalin and trans-decalin, each with a different value of θ. Two authors have evaluated K, namely, Berry[13] and Fukuda et al.[2] As shown in Table 6, Berry found a value of 82.4×10^{-3} mL/g for K for cis-decalin at 12.2 °C and for trans-decalin, Fukuda et al. found θ to be 20.4 °C with a value of K of 80.5×10^{-3} mL/g.

2.11. Other Solvents

Data are available for several other solvents, but since only one set is usually available per solvent, no critical comparison was possible. The values are listed in Table 4.

2.12. Recommended Values of K and a

The recommended values of K and a for the most frequently used solvents are given in Table 7.

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